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SHORT COMMUNICATION

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Prediction of nitrogen, active carbon, and organic carbon-to-clay ratio in agricultural soils by in-situ spectroscopy

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Abstract

Visible and near-infrared (vis–NIR) spectroscopy is a promising technology for the analysis of different soil quality parameters. In this study, we used in-situ vis–NIR spectroscopy in association with partial least squares regression to predict the total and the mineral (nitrate + ammonium) nitrogen content, the permanganate oxidizable carbon (POXC), as well as the ratio of soil organic carbon-to-clay content in different agricultural soils in Switzerland. These parameters can indeed be used as indicators of soil quality in response to agronomic practices. To this goal, a total number of 134 soil samples were used for carbon-, total nitrogen- and clay-related parameters, whereas 69 soil samples were used for the mineral nitrogen-related parameters. We found that the partial least squares regression model can successfully predict the total nitrogen and the POXC content as well as the ratio of soil organic carbon-to-clay content (ratio of performance to interquartile range, RPIQ > 2.62, R^2 > 0.73, Lin's concordance correlation coefficient > 0.83). As concerns the mineral nitrogen, it was not possible to successfully predict this parameter by vis–NIR spectroscopy. By demonstrating the possibility to reliably predict POXC content and the soil organic carbon-to-clay ratio, we show that vis–NIR can be also used to analyse soil parameters associated with both the quality of organic carbon and the structural quality of agricultural soils.

KEYWORDS

Nmin, PLSR, POXC, proximal soil sensing, SOC:clay ratio, vis–NIR

1 | INTRODUCTION

Nitrogen (N) is a crucial element for crops, but it has also negative environmental impacts when lost into the environment (Guerrero et al., 2021). Nitrogen exists in two main forms in the soil, i.e., as organic and inorganic N, which change dynamically through nitrification, denitrification, mineralisation, immobilisation and volatilisation. Most of total soil N (over 90%) is found within the organic matter (i.e., as organic N) where it is immobilised primarily in form of proteins that, once mineralised, can become a source of plant-available N (Bingham &

Cotrufo, 2016; Li et al., 2014). In the mineral form of nitrate (NO_3^-), N is readily available for plants and microbes, but it is also soluble and can be leached. In the mineral form of ammonium (NH_4^+), N is available to the plants usually after nitrification but, differently from nitrate, it can be absorbed on soil particles depending on soil cation exchange capacity (Fowler et al., 2013; Grossrieder et al., 2022; Guerrero et al., 2021; Podlasek et al., 2021; Sinaj et al., 2017). To optimize the N fertilization for crops, the quantification of the amount of soil mineral N (i.e., $NO_3^- + NH_4^+$) or, more generally, the soil capability to provide plant-available N is crucial for a site-specific strategy of nutrient management that aims at both improving crop N use efficiency and reducing the environmental losses (Mahmud et al., 2021).

Soil organic carbon (SOC) is crucial for crop nutrition as well as for storing atmospheric C (Gerke, 2022; Minasny et al., 2017). Although the amount of SOC in agricultural soils is considered a primary indicator of soil quality (Krause et al., 2022), SOC reacts very slowly to any practice aiming at increasing its concentration and stock (Bongiorno et al., 2019; Pulleman et al., 2021). An alternative approach to investigate SOC content is to look at the different forms of SOC, such as permanganate oxidizable carbon (POXC), also called active C (Culman et al., 2012; Wade et al., 2020). This SOC form represents the fraction of SOC that is biologically active, i.e., readily available for soil life and highly involved in SOC cycling (Awale et al., 2017; Stott, 2019). A study conducted by Vonk et al. (2020) did not find a clear correlation between increased SOC and yield, but Weil et al. (2003) showed a positive correlation between POXC and yield among other soil quality indicators.

In agricultural soils, SOC also affects multiple physical properties, such as bulk density, water holding capacity and hydraulic conductivity (Palmer et al., 2017). To characterise the physical quality of agricultural soils, the ratio of the SOC content (g/100 g) to clay content (g/100 g), i.e., the SOC:clay ratio, has been proposed as an indicator of soil structural stability or soil degradation (EEA—European Environment Agency, 2023; Johannes, Matter, et al., 2017; Prout et al., 2021), being well correlated with the scores of soil structural quality assessment, i.e., the CoreVESS (Johannes, Weisskopf, et al., 2017). Accordingly, a SOC:clay ratio of 1:8 (= 0.12) is suggested as a threshold for optimum soil structure, whereas a SOC:clay ratio <1:13 (< 0.07) indicates an unacceptable soil structural quality (Johannes, Matter, et al., 2017). A SOC:clay ratio of >1:10 (i.e. >0.1) can also be used as a target to aspire to when increasing the amount of C in arable soils for C sequestration, whereas soils with a good SOC:clay ratio of 1:8 might be prone to SOC losses (Guillaume et al., 2022; Johannes et al., 2023; Prout et al., 2021, 2022).

In recent decades, visible and near-infrared (vis–NIR) spectroscopy has emerged as a technique for a rapid characterisation of some chemical and mineralogical parameters related to soil fertility (Ahmadi et al., 2021; Barra et al., 2021; Zeng et al., 2022). The best calibration models linking soil spectra with laboratory analyses are usually obtained for SOC, clay content, and total nitrogen (Ntot) (Guerrero et al., 2021; Nawar & Mouazen, 2017; Nocita et al., 2015; Stenberg et al., 2010; Viscarra Rossel et al., 2022). This is due to the interaction of vis–NIR radiation (350–2500 nm) with chemical bonds such as C–H, O–H, C–N that make up the soil parameters listed above (Ben-Dor & Banin, 1995; Nocita et al., 2015). In addition, other studies have also reported a rather good relationship for other parameters such as extractable macronutrient concentration, iron and iron oxides, pH and cation exchange capacity (Barra et al., 2021), even though it is still under debate to what extent vis–NIR spectroscopy provide reliable information for some of these parameters (McBride, 2022; Viscarra Rossel et al., 2022). However, concerning the possibility to predict the amount of different N forms by vis–NIR spectroscopy, the results are sometimes contradictory (Fystro, 2002; Soriano-Disla et al., 2014; Stenberg et al., 2010). Recently, Chen et al. (2022) conducted a small-scale study where they mixed different types of fertilizers with two soil types and were able to predict the levels of N fertilizer based on vis–NIR imaging spectroscopy, whereas Tsakiridis et al. (2017) successfully predicted the amount of NO_3^- from diffuse reflectance spectra. These studies showed promising results on dried soils and raise the question about whether good correlations can be found with vis–NIR spectra recorded in situ. Contrarily, Guerrero et al. (2021) stated that only total N can be predicted with vis–NIR but not the N mineral forms. With regard to POXC, still a limited number of studies have predicted POXC with vis–NIR spectroscopy. For example, Calderon et al. (2017) found good correlations between spectra from dried and sieved soil samples suggesting to further examine the possibility of detecting POXC using in-situ portable vis–NIR spectrometers. With its potential to show dynamic changes incurred by management practices, POCX is a helpful indicator for soil health (Stott, 2019) and a reliable prediction from vis–NIR spectra would greatly benefit its applicability. To our knowledge, no study has tried to predict the SOC:clay ratio directly from in-situ vis–NIR spectra, while numerous studies have already been able to predict SOC and clay separately by spectroscopy (e.g., Ahmadi et al., 2021; Metzger et al., 2023). Considering that this ratio has been recently included into the European Union soil monitoring framework (EEA—European Environment Agency, 2023), it would be helpful to assess if the error is smaller when the SOC:clay ratio is predicted directly from vis–NIR spectra as compared to calculating the ratio from already predicted SOC and clay values.

The main goal of this study is to test the possibility to predict nitrate, ammonium, mineral N, easily oxidizable C and the SOC:clay ratio based on vis–NIR spectra directly collected in the field, i.e., in-situ. We hypothesise that, due to the chemical composition, the mineral forms of N, i.e., Nmin, NO_3^- and NH_4^+, cannot be satisfactorily predicted even from field-collected soil spectra, whereas the amount of POXC and the soil structural quality (i.e., the SOC:clay ratio) can be reliably predicted by in-situ vis–NIR spectroscopy.

2 | MATERIALS AND METHODS

2.1 | Soil samples

During a sampling campaign in 2021, 134 soil samples were collected from nine long-term experimental trials in Switzerland to include a wide variety of tillage practices (i.e., from plough tillage to no-till), fertilisation inputs (no fertilisation, mineral fertilisers only and organic fertilisers only), and crop rotations (monocropping and rotation) under different physico-chemical characteristics (i.e. texture, SOC content, pH). A detailed description of the experimental trials can be found in the Table S1, whereas a description of the correspondent soil types and geographical locations can be found in Metzger et al. (2023). Soil samples were collected using an Edelman auger (Eijkelkamp, NL) at a depth of 0–20 cm at the centre of each treatment plot.

2.2 | Laboratory analyses

After sampling, the soil samples were dried (40°C × 24 h) and then sieved at 2 mm for further analyses. Soil moisture content (105°C × 24 h) was determined gravimetrically on a subsample of fresh soil and the following physico-chemical parameters were analysed: clay content, SOC, POXC, Ntot, NO_3^-, and NH_4^+. The clay content was determined using the pipette method (Gee & Bauder, 1986), the SOC content by sulfochromic oxidation (NF ISO 14253), and the Ntot by dry combustion using an elemental analyser (NF ISO 13878). The concentration of POXC was determined following the protocol by Weil et al. (2003) and Culman et al. (2014) in which the readily available C (= active C) is oxidised with 0.02 M $KMnO_4$. The concentration of nitrate and ammonium was measured according to the indophenol blue colorimetric method (Ringuet et al., 2011) and the Griess reaction (Doane & Horwáth, 2003) in a subset of 69 soil samples from four trials that were immediately frozen after field sampling until analysis. A more detailed description of the measurements of POXC, nitrate and ammonium can be found in the Supporting information.

2.3 | Spectral measurements and processing

Vis–NIR spectra of soil samples were taken in-situ according to the protocol proposed by Metzger et al. (2023). Briefly, after the sampling of the soil, one side of the Edelman auger was smoothed with a knife and five replicate scans were performed over the entire side of the soil core. The scans were performed by means of a contact probe with a 5 W tungsten-halogen lamp using a Spectral Evolution PSR+ 3500 portable spectrophotometer (Spectral Evolution, Haverhill, MA, USA) characterised by a spectral range of 350–2500 nm and a spectral resolution of 2.8–8 nm.

The raw spectra were reported in reflectance with a wavelength interval of 1 nm. In order to check the stability of the five replicate scans, the spectral standard deviation was calculated according to Metzger et al. (2020) and only when the spectral deviation was below 0.01 then all the spectra were included. In our case, all the five replicate scans were accepted. We would like to underline that, for the goals of this study, the spectra were not processed further to remove the influence of soil moisture (e.g. external parameter orthogonalisation or direct standardisation).

2.4 | Calibration models

In order to relate the laboratory results to the spectral information, partial least squares regression (PLSR) was applied to predict SOC, clay content, Ntot, Nmin, NO_3^-, NH_4^+, POXC, and SOC:clay ratio: (Barra et al., 2021; Wold, 1973). We used a 100-times repeated double-cross--validation approach to prevent over optimistic model performances (Filzmoser et al., 2009) and the number of latent variables for the PLSR was determined by selecting the model with the first minimum of the standard error of prediction for each soil property and spectral preprocessing. Spectral preprocessing methods are used to better extract the signal in the spectra and contain both smoothing and derivatives (Savitzky–Golay smoothing and first and second derivatives; see Savitzky & Golay, 1964), normalization (Standard Normal Variate

SNV; see Barnes et al., 1989) and multiplicative scatter correction or MSC (Geladi et al., 1985). A more detailed description of the model can be found in Metzger et al. (2023). The best model for each parameter was then chosen based on the following model parameters: coefficient of determination (R^2), root mean squared error of the prediction (RMSEP), ratio of performance to interquartile range (RPIQ = IQR/RMSE, IQR = Q3 − Q1), the bias and Lin's concordance correlation coefficient (CCC) (Mendes et al., 2021). All data analysis was performed in R version 4.1.3 (R Core Team, 2022) and the used packages are listed in the Supporting information.

3 | RESULTS

The variability of the selected chemical and physical soil parameters spans a range representative of main conditions of agricultural soils in Switzerland (see the Table S2 for a summary). The results for the PLSR model are in Table 1. For clay, SOC and Ntot the PLSR shows acceptable values of R^2, RMSEP, RPIQ and Lin's CCC, with R^2 and Lin's CCC being close to 1, and RPIQ >1.89 (Ludwig et al., 2019). Nmin and NO_3^- show somewhat promising results (RPIQ > 1.86, but Lin's CCC < 0.8 and $R^2 \leq 0.62$) while for NH_4^+ the indicators of model performance are unfavourable. The content of POCX is also successfully predicted based on the values of RMSEP (96.5), R^2 (0.75), RPIQ (2.71), bias (0.13) and Lin's CCC (0.86). The SOC:clay ratio was initially predicted directly and then it was also calculated from the individually predicted SOC and clay values. For the directly predicted ratio, the PLSR model is able to successfully predict the SOC:clay ratio, considering the values of RMSEP (0.01), R^2 (0.73), RPIQ (2.62), bias (<0.01) and Lin's CCC (0.83). The individually predicted SOC:clay ratio shows a lower performance, with a low Lin's CCC of 0.75 and R^2 of 0.55. The predicted versus the reference values of all the studied soil parameters are plotted in Figure 1. An overview over the model parameters is also given in Table S3.

4 | DISCUSSION

In accordance with previous studies (e.g., Debaene et al., 2023; Guerrero et al., 2021; Viscarra Rossel et al., 2009; Wang et al., 2021), we confirm that it is possible to reliably predict the amount of clay, the content of SOC and the content of total N from in-situ spectra. The prediction of soil Ntot content by vis–NIR spectroscopy from in-situ spectra is particularly important in terms of site-adapted fertilisation considering the importance of organic N pool for the provision of available N to crops (Farzadfar et al., 2021; Mittermayer et al., 2021; Yan et al., 2020). Such good predictive performance can be explained by the strong correlation between Ntot and SOC content (partial correlation coefficient = 0.98, $p < 0.01$, $n = 134$). The prediction of NO_3^- with R^2 of 0.62 and RPIQ of 2.18 shows some potential, even if in the laboratory versus the reference plots show two clear clusters that may have artificially improved the performance (Figure 1). Additionally, an unsuccessful prediction of NH_4^+ (RPIQ 1.16) means that the use of vis–NIR for Nmin prediction remains unattainable. Our results, although based on a relatively low number of soil samples, seem in line with other works reporting a possible prediction of nitrate using vis–NIR spectroscopy from sieved and dried soil samples (Amirul et al., 2020; Ehsani et al., 1999; Zhou et al., 2023), whereas ammonium was only reliably predicted by vis–NIR in soil pore-water samples (Yupiter et al., 2023). Further studies are necessary to better clarify the possibility to predict nitrate content in agricultural soils based on in-situ vis–NIR spectroscopy.

TABLE 1 Model performance indicators, i.e., root mean squared error of prediction (RMSEP), coefficient of determination (R^2), ratio of performance to interquartile distance (RPIQ), Lin's concordance coefficient (CCC) and bias for the studied soil parameters.

Parameter	R^2	R^2_sd	RMSEP	RMSEP_sd	RPIQ	RPIQ_sd	Lin's CCC	Lin's_sd	Bias	Bias_sd
Nmin (mg/kg)	0.62	0.027	5.58	0.191	2.03	0.067	0.77	0.016	0.04	0.115
NO_3^- (mg/kg)	0.59	0.033	4.67	0.183	2.18	0.080	0.75	0.021	0.04	0.116
NH_4^+ (mg/kg)	0.37	0.031	1.89	0.046	1.16	0.028	0.56	0.022	0.01	0.024
Clay (%)	0.94	0.004	3.27	0.095	4.63	0.131	0.97	0.002	0.01	0.061
SOC (%)	0.82	0.015	0.30	0.012	3.13	0.120	0.89	0.009	0.00	0.008
Ntot (%)	0.79	0.009	0.04	0.002	3.10	0.123	0.87	0.012	0.00	0.001
SOC:clay_directly	0.73	0.001	0.01	<0.001	2.62	0.106	0.83	0.015	0.00	<0.001
SOC:clay_individually	0.55		0.01		2.12		0.75		0.00	
POXC (mg/kg)	0.75	0.011	96.42	2.054	2.71	0.056	0.86	0.007	0.13	2.153

Note: For each accuracy metrics of each parameter, the standard deviation (sd) resulting from the 100 repetitions is reported.

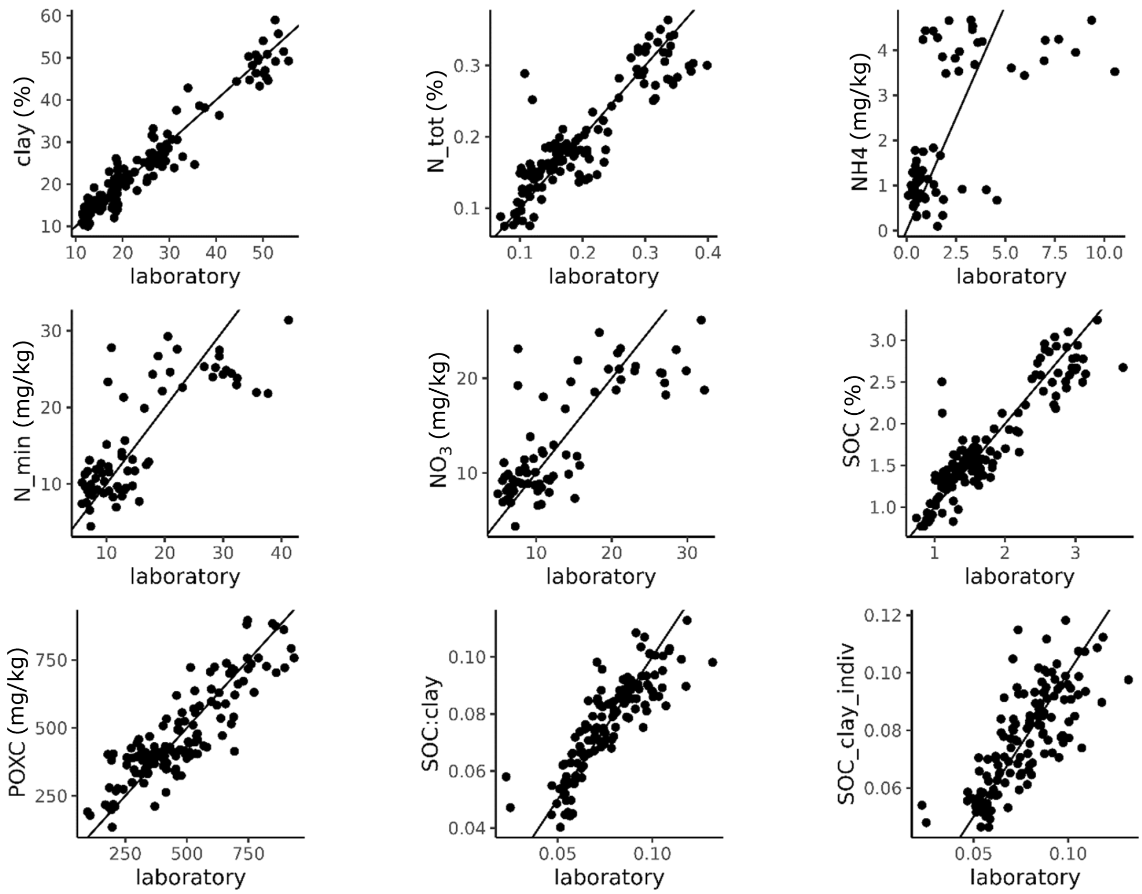

FIGURE 1 Laboratory versus partial least squares regression predicted values for clay (%), total nitrogen (Ntot) (%), NH_4^+ (mg/kg), Nmin (mg/kg), NO_3^- (mg/kg), soil organic carbon (SOC) (%), permanganate oxidizable carbon (POXC) (mg/kg), the directly predicted SOC:clay ratio as well as the calculated SOC:clay ratio from previously predicted SOC and clay values (SOC_clay_indiv). The 1:1 line of equality is reported.

For the POXC, our results indicate that vis–NIR spectroscopy can well predict the amount of soil active C (Calderon et al., 2017; Omer et al., 2020; Reijneveld et al., 2023). As previously observed (e.g., Plaza-Bonilla et al., 2014), in our dataset, there was a positive correlation between SOC and POXC ($r = 0.88$) suggesting that, as recently highlighted by Woodings and Margenot (2023), POXC may indeed reflect a more processed fraction of soil C. After taking into account the standardization of analytical methods for measuring POXC in soil samples (Wade et al., 2020), the reliable estimation of POXC by vis–NIR can represent a helpful tool to easily follow the temporal and spatial trends of a soil quality indicator that is expected to react more rapidly to agronomic management (Lucas & Weil, 2021; Plaza-Bonilla et al., 2014; Singh et al., 2023; Zhao et al., 2022).

Our study clearly shows that SOC:clay ratio can be reliably predicted by in-situ vis–NIR spectroscopy with better results in terms of R^2, RPIQ and Lin's CCC compared with an indirect calculation based on individual prediction of SOC and clay values. This result can be explained by a lower error propagation. Indeed, looking at the plot of both types of SOC:clay prediction (Figure 1) it is clear that the individually predicted values deviate much more from the 1:1 line, very likely due to the added inaccuracy from the individual predictions of both SOC and clay.

5 | CONCLUSIONS

Our study shows that the SOC:clay ratio as well as the POXC content can be successfully predicted from in-situ vis–NIR soil spectra. This opens the possibility to use in-situ soil spectroscopy to predict additional soil indicators that are related, respectively, the active forms of SOC and the structural stability of agricultural soils.

AUTHOR CONTRIBUTIONS

Konrad Metzger: Conceptualization (equal); formal analysis (lead); investigation (lead); writing – original draft (equal); writing – review and editing (equal). **Luca Bragazza:** Conceptualization (equal); formal analysis (supporting); investigation (supporting); project administration (lead); supervision (lead); writing – original draft (equal); writing – review and editing (equal).

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CONFLICT OF INTEREST STATEMENT

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

DATA AVAILABILITY STATEMENT

The datasets and R scripts for this study are available upon request from the authors.

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